

Polymer Microspheres Studied by X-ray Spectromicroscopy

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INTRODUCTION

Polymer microspheres with internal structure are used in a number of applications, including separation science applications, coatings, adhesives, chemical delivery etc [1]. In order to optimize structured microspheres for particular applications such as chromatography beads, it is useful to quantitate the chemical structure at high spatial resolution. We use STXM and soft X-ray spectromicroscopy techniques for this purpose. STXM is a powerful tool for sub micron analysis of polymers [2,3]. NEXAFS spectroscopy at high spatial resolution and energy selective imaging provide sensitivity to many sample properties such as local chemical composition, orientation, adsorbate-substrate relationships, etc. The intrinsic power of STXM spectromicroscopy is further enhanced by acquisition strategies such as linescans, image sequences, as well as sophisticated analysis methodologies which simultaneously exploit the spatial and spectral domains to achieve composition mapping [4]. Such procedures can be based on singular value decomposition [5], multivariate statistical analysis or linear regression procedures. Here we use results from studies of polymer microspheres to illustrate the polymer microanalysis capabilities of STXM.

QUANTITATIVE ANALYSIS OF POLYMER MICROSPHERES

To calibrate STXM capabilities we have studied a series of core-shell microspheres in which a ~4 μm core is precipitation polymerized from DVB55 (55% divinylbenzene / 45% ethylvinylbenzene) followed by a second precipitation polymerization of a ~300 nm shell from mixtures

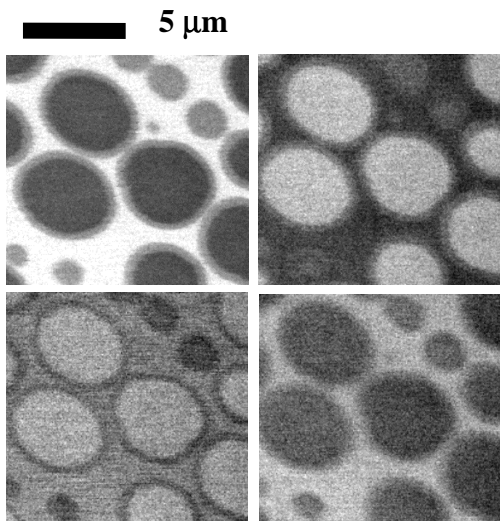


Figure 1 STXM images at 285, 288.2, 288.4 and 305 eV of microspheres composed of a DVB55 core and a shell which is 70 v/v% EGDMA/30% DVB55. The ~5 μm diameter microspheres are embedded in an epoxy which is similar to EGDMA. A 0.2 eV shift near the strong $\pi^*(\text{C}=\text{O})$ peak readily distinguishes shell and epoxy components.

of DVB55 and EGDMA (ethyleneglycol-dimethacrylate) where the EGDMA content ranges from 10 - 100%. These cross-linking polymers allow flexible control of porosity. Cross-sectional TEM readily reveals the core-shell structure but cannot distinguish chemical from density/thickness variations. STXM images at selected energies, as shown for a 70% EGDMA shell microsphere in **Figure 1**, differ dramatically in core-shell contrast, providing a basis for quantitative analysis of the composition of the shell.

Figure 2 displays the C 1s NEXAFS spectra of the three chemical components of this system, poly-DVB55, poly-EGDMA, and the aliphatic Spurr's epoxy resin used to embed the microspheres for microtoming.

Sets of images were inverted using singular value decomposition (SVD) [5] to generate quantitative component maps of the poly-DVB55 and poly-EGDMA from which the composition of the shell through the series was evaluated (**Figure 3**).

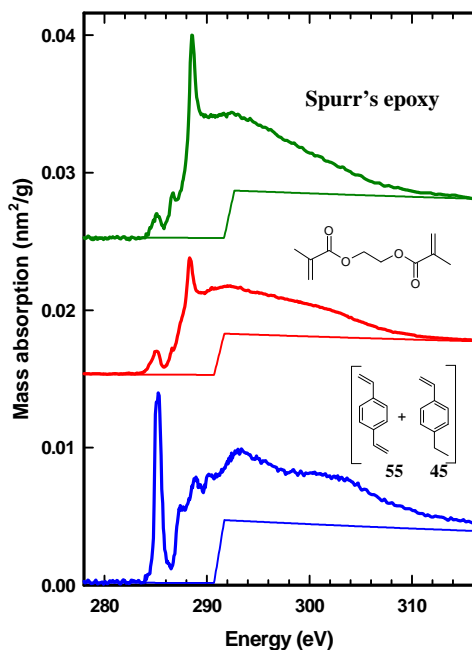


Figure 2 Reference spectra (mass thickness scale) used to generate composition maps.

Since optical density, $OD = \log_{10} (I_0 / I) = \alpha pt$ is directly proportional to mass thickness (pt), linear algebra can be used to convert images into equivalent thickness or composition maps. In principle, the decomposition problem can be expressed as a matrix equation $Ax=d$, where x is a vector describing the unknown distribution (pt), d are the measured images (converted to an optical density (OD) scale), and A is the matrix of mass thickness coefficients (α). The mass thickness coefficients for polyDVB55 and polyEGDMA at 281.0, 285.1, 288.3 and 305.0 eV were obtained from near-edge absorption spectra of the pure materials, extracted from the microsphere sample with a shell of 100% EGDMA, and converted to mass absorption scales by matching the spectrum below 282 eV and above 310 eV to the curves for the elemental compositions [6]. In this case, because the epoxy and the EGDMA C 1s spectra are rather similar (a different epoxy would make a cleaner

separation), we have used only the DVB-55 signal to quantify the shell composition, assuming the remainder is EGDMA. In fact, there appears to be some (<10 %) penetration of the epoxy into the shell and core regions. However, if the degree of penetration is similar, then the DVB-55 amount should quantitate the shell composition. This appears to be the case, since the shell composition determined by STXM is in good agreement with that predicted from the synthesis.

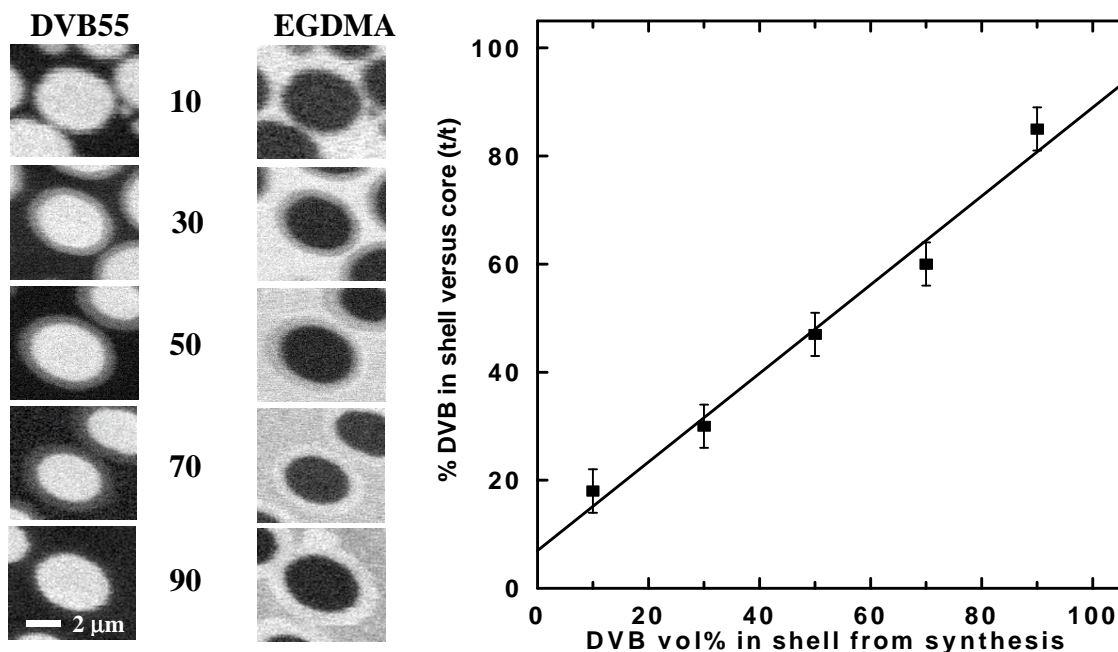


Figure 3 (left) DVB55 and EGDMA component images for 10 - 90 v/v % EGDMA shell composition, derived from SVD analysis of images at 281.0, 285.1, 288.3, and 305.0 eV. The intensity of the shell region shows changing concentration of each species. (right) %DVB in the shell relative to the core derived from the DVB55 composition maps. The correlation with the synthesis prediction assumes the core is 100% DVB55 and the shell is a variable mix of DVB55 and EGDMA.

A full report on the quantitative analysis will appear elsewhere [7]. Clearly STXM can provide excellent quantitative analysis of polymers at the 100 nm size scale. We are in the process of extending our analysis to separate the epoxy and EGDMA components in order to measure the diffusion of epoxy into core and shell. If successful, this will allow us to map the porosity in the core and shell regions, which is of considerable interest with regard to developing a better understanding of the relationship of internal structure and the performance of structured polymer such as these microspheres in targeted applications.

SUMMARY

The good spatial resolution, high chemical sensitivity and applicability to radiation sensitive materials such as polymers give STXM unique advantages relative to other techniques. In the near future, improvements in zone plate technology, the upgrade of the BL 7.0 STXM, and improved access via completion of the 5.3 STXM beam line, will provide improved performance and allow extensive exploitation of STXM for polymer microanalysis.

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